# Residues of O,P′-DDD and O,P′-DDT in Brown Pelican Eggs and Mallard Ducks

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Annual use of technical DDT in the United States has exceeded 40 million pounds per year since 1949 (1). Since o,p'-DDT constitutes approximately 15-20 percent of technical grade DDT, this represents an annual use of 6-8 million pounds. Although all specimens of wild birds analyzed at this laboratory in the past six years have contained p,p'-DDE and many have contained p,p'-DDT or p,p'-DDD, we have only rarely found o,p'-DDT and have never detected the metabolite o,p'-DDD. A biological isomeric transformation of o,p'-DDT to p,p'-DDT was reported by Klein et al. (2) from studies with rats, and French et al. (3) found some evidence of such a conversion in living pigeons (Columbia livia). This change, if prevalent, could explain the rarity of the o,p' isomers in biological material.

The purpose of this paper is to report the presence of o,p'-DDD in mallards (Anas platyrhynchos) fed pure o,p'-DDT and in brown pelican eggs (Pelecanus occidentalis) collected in the field. The pelican eggs also contained unusually high concentrations of o,p'-DDT.

## Sample Data

The brown pelican eggs were collected from nests on Anacapa Island, California, in April 1969 in conjunction with a study of the colony's nesting failure. Ten specimens were shipped frozen, were stored in a freezer at -27°C for 2 weeks, and then were analyzed. None of the eggs appeared to be addled, dried, or to contain embryos. The mallard ducks were sacrificed after 10 weeks on a diet containing 25 ppm of o,p'-DDT. The toxicant was dissolved in corn oil, which constituted 1 percent of the diet. The control birds received an equal amount of clean oil. The specimens were stored in the freezer for 3 months before analysis.

The toxicant fed to the mallards was checked for the presence of o,p'-DDD by streaking 100 μg on a thin layer (TL) plate and removing the o,p'-DDD zone from the plate. This fraction was eluted and subjected to a gas chromatographic analysis, which showed no o,p'-DDD; limit of detection was 0.05%.



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## Analytical Procedure

Liver and breast muscle samples from the mallards and the contents of the pelican eggs were prepared and cleaned up as previously described by Reichel et al. (4). Briefly, this method consists of Soxhlet extraction, cleanup by acetonitrile partitioning, and Florisil column. The residues were separated and removed in four fractions from a silica gel TL plate by the method described by Mulhern (5). All sample fractions were analyzed by electron capture chromatography on a 3% OV-17 column and confirmed on a 12% DEGS column and on a 3% XE-60 column. The operating conditions are shown in Table 1. When this procedure is followed, polychlorinated biphenyl (PCB) compounds do not interfere with the proper identification or quantification of the chlorinated pesticides.

TABLE 1
Chromatographic Operating Conditions
Using Electron Capture Detector

| | Columns, glass 6" x ¼ " OD | | |
|---|---|---|---|
| | A | B | C |
| Liquid phase | 3% OV-17 | 3% XE-60 | 12% DEGS |
| Solid support | Gas chrom Q | Gas chrom Q | Anakrom SD |
| Mesh size | 100/120 | 60/80 | 100/110 |
| $N_2$ Flow rate | 100 | 100 | 85 |
| Temp. $^oC$ | 200 | 170 | 200 |
| Retention time of Dieldrin, min. | 9 | 17 | 9.5 |

In addition, the appropriate TL fractions from the extracts of the brown pelican eggs were treated with alkali to confirm the presence of o,p'-DDD, p,p'-DDD, o,p'-DDT, and p,p'-DDT by conversion to the corresponding olefin.

## Gas Chromatograph-Mass Spectrometer

Positive identification of o,p'-DDD in the mallards and of o,p'-DDD, o,p'-DDT, and PCB's in some of the pelican eggs was accomplished with the use of a LKB 9000 gas chromatograph-mass spectrometer equipped with the stainless steel, molecule separator

system of Ryhage (6), and a spiral glass column (9' x 0.25") packed with 1% SE-30 on 100/120 mesh Gas Chrom Q. Operating conditions were: flow rate 35 ml/min. of helium; oven temp. 180°C; flash heater 220°; separator 240°C; and ion source 270°C. The ionization potential was 70 eV, trap current 60 μA and accelerating voltage 3.5 KV.

The mass spectra obtained from the samples were compared with mass spectra obtained from reference solutions of o,p'-DDD, o,p'-DDT, and a commercial preparation of PCB, Arochlor 1254.

## Results and Discussion

Results of analysis of the pelican eggs are shown in Table 2. In addition to the high residue levels of DDT and metabolites, the eggs contained PCB compounds. Residues of o,p'-DDD have not previously been reported in wildlife specimens. The detectable level of o,p'-DDD is probably related to the presence of unusually high levels of o,p'-DDT. This indicates that when o,p'-DDT is detected in a sample the analyst should choose a GC column that will separate the o,p'-DDD metabolite. Results of analysis of tissues of mallards fed o,p'-DDT are shown in Table 3. Within the limits of detection, residues of p,p'-DDE, p,p'-DDT, and p,p'-DDD were the same in the tissues of controls as in tissues of birds fed o,p'-DDT. Since there was no increase in levels of p,p'-DDT or its metabolites, the biological isomeric transformation evidently did not take place. The o,p'-DDD detected in the mallards and pelican eggs may have metabolized from o,p'-DDT in the living specimen or may have been postmortem breakdown product as indicated by French et al. (3). Further research is needed to explain the low residue levels in mallards receiving a dietary dosage of 25 ppm of o,p'-DDT for 10 weeks.

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TABLE 2

Residues in Brown Pelican Eggs

| Egg No. | Weight (gms) Contents | Residue content, ppm wet weight | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | p,p'-DDE | p,p'-DDD | p,p'-DDT | Dieldrin | o,p'-DDT | o,p'-DDD | PCB(1) |
| 1 | 100.1 | 76.1 | 1.3 | 1.9 | 0.2 | 0.08 | 0.08 | + |
| 2 | 99.3 | 50.6 | 1.4 | 1.9 | 0.1 | 0.1(1) | 0.2(1) | + |
| 3 | 114.7 | 135.0 | 2.4 | 3.8 | 0.2 | 0.1 | 0.2 | + |
| 4 | 99.2 | 60.2 | 0.3 | 0.6 | <0.08 | <0.08 | ND | + |
| 5 | 91.5 | 39.5 | 0.5 | 1.2 | <0.07 | <0.07 | <0.07 | + |
| 6 | 97.6 | 97.8 | 3.4 | 4.6 | 0.1 | 0.5 | 0.2(1) | + |
| 7 | 88.0 | 63.2 | 1.3 | 1.6 | 0.08 | 0.2(1) | 0.2(1) | + |
| 8 | 97.9 | 65.0 | 0.9 | 1.5 | 0.07 | <0.08 | <0.08 | + |
| 9 | 106.6 | 70.0 | 1.3 | 1.4 | 0.08 | 0.1 | 0.08 | + |
| 10 | 78.4 | 98.4 | 1.5 | 1.9 | 0.2 | 0.1 | 0.1 | + |

(1) Compounds were confirmed by GLC-mass spectrographic analysis.

TABLE 3

Residues in Tissues of Mallard Ducks Fed o,p'-DDT

| Bird No. | Tissue | Residue content, ppm wet weight | | | | |
|---|---|---|---|---|---|---|
| | | p,p'-DDE | p,p'-DDD | p,p'-DDT | o,p'-DDT | o,p'-DDD |
| Control(1) | Liver | T | T | T | ND | ND |
| | Br. Muscle | T | ND | T | ND | ND |
| 1 ♀ | Liver | T | T | T | <0.03 | 0.3(2) |
| | Br. Muscle | T | T | T | <0.05 | <0.1 |
| 2 ♀ | Liver | T | T | T | <0.03 | 0.2 |
| | Br. Muscle | T | T | T | 0.09 | 0.1 |
| 3 ♂ | Liver | T | T | T | <0.02 | 0.3(2) |
| | Br. Muscle | T | T | T | <0.05 | 0.09 |
| 4 ♂ | Liver | T | T | T | <0.03 | 0.2 |
| | Br. Muscle | 0.09 | T | T | <0.07 | 0.2 |
| 5 ♀ | Liver | T | T | ND | ND | <0.07 |
| | Br. Muscle | T | T | ND | <0.03 | 0.1 |

T = <0.05 ppm ND = Not detected

(1) Pool of two samples

(2) The presence of o,p'-DDD was confirmed by mass spectrographic analysis.

## References


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